

29 algebraically independent invariants ; while, if only a single function ϕ occurs, all the invariants that occur up to the second order can be expressed in terms of 20 algebraically independent invariants.

The significance of these respective aggregates of 29 and of 20 invariants is obtained in connection with curves

$$\phi = 0, \psi = 0,$$

drawn upon the surface. The investigation reveals new relations among the intrinsic geometric properties of a curve upon a surface. In particular, up to the second order, four such relations exist for a single curve ; and their explicit expressions have been constructed.

“The Electrical Conductivity of Solutions at the Freezing-point of Water.” By W. C. D. WHETHAM, F.R.S., Fellow of Trinity College, Cambridge. Received February 14,—Read March 5, 1903.

The following paper contains an account of experiments which bring to greater concentrations the series of measurements on the conductivities of dilute solutions at the freezing point, communicated to the Royal Society in February, 1900.* The work has been carried on at intervals during the last two years, and was made possible by the kindness of Professor Ewing, who placed a room at the Cambridge Engineering Laboratory at the disposal of the writer and his wife.

The earlier experiments were originally planned in connection with the observations undertaken by Dr. E. H. Griffiths on the freezing points of corresponding solutions ; they were therefore conducted in a platinum cell of design similar to that used by Griffiths, with the object of eliminating any solvent action of glass. Any such action would be quite inappreciable at the concentrations used in the experiments now to be described ; resistance cells of glass were consequently used, and the labour of observation was much reduced.

The structure of the cells is shown in figs. 1 and 2 ; that illustrated in fig. 1 was made of Jena glass, and reserved for the more dilute solutions. Each cell is so arranged that by applying a slight exhaustion, the whole of the contents can be drawn up into a bulb ; by this means, when water or stock solution is added, complete mixture can be easily secured. The method of preparing the solutions was usually the same as that formerly employed ; the pure solvent was placed in the cell, and its weight and resistance determined ; weighed quantities

* ‘Phil. Trans.,’ A, vol. 194 (1900), p. 321.

of stock solution were then added successively, the resistance being measured after each addition. When, however, the solutions approached saturation, this procedure was reversed ; the stock solution was first examined, and was then diluted by a weighed quantity of water.

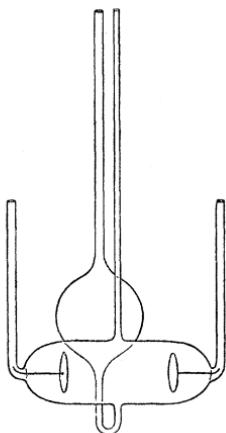


FIG. 1.
($\frac{1}{4}$ full size.)

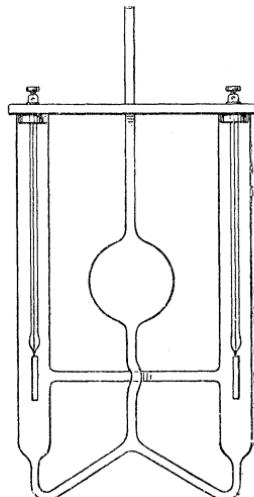


FIG. 2.
($\frac{1}{4}$ full size.)

The resistance cell was placed in a tin bath filled with melting ice. At first, a thermometer was inserted in the cell, and the observations postponed till its readings became steady at 0° centigrade ; but it was soon found that the resistance itself gave a more sensitive and convenient means of thermometry. Measurements were taken at intervals till they became constant ; the cell being always completely immersed in ice, the result thus obtained shows the resistance at 0° . As an example, the following numbers may be given :—

| Time. | Resistance. |
|-------|-------------|
| 12.45 | 2179 |
| 12.55 | 2191 |
| 1.12 | 2202 |
| 1.16 | 2202 |
| 1.18 | 2202 |

It was intended to make up the solutions in the resistance cell while it was immersed in the ice, but condensation of water from the atmosphere was found to occur on the inside of the cold vessel when stock solution was added. Before each addition, therefore, the cell and its contents were raised to some temperature near that of the

room by standing the cell for a few minutes in slightly warmed water.

The water used as solvent was first boiled, then distilled in glass from alkaline permanganate, and finally redistilled in a platinum still with a trace of acid potassium sulphate. It was kept in a large stoppered flask of Jena glass till required for the experiments.

The samples of salt used to make the stock solutions of potassium chloride and copper sulphate were the same as those prepared for the earlier experiments; details will be found in the account of those experiments to which reference has already been made. In the cases of barium chloride, potassium bichromate, and magnesium sulphate, the best salt, sold as chemically pure, was obtained, the two salts first mentioned being recrystallised before use. Any probable impurities would not affect the results to an amount equal to the other errors of experiment.

The measurement of the electrical resistance was performed exactly as in the earlier set of experiments. The current from one or two dry cells was alternated by means of a revolving commutator, which was driven by a hand wheel and cord, the connections of a D'Arsonval galvanometer being simultaneously alternated by the same instrument. The alternating currents were passed through a Wheatstone's bridge, in one of the arms of which was inserted the electrolytic cell. This apparatus worked with perfect success; its sensitiveness was enough to enable readings to be taken to an accuracy varying from one part in one thousand to one part in thirty thousand, according to the resistance in the circuit.

The results which were obtained are collected below. In the table headed Potassium Chloride I, and in the tables for all the other salts, the concentrations, given in the first column under m , are calculated in terms of the number of gram-equivalents of salt per thousand grams of solution, while, for the sake of comparison, under Potassium Chloride II, the conductivities are reckoned per thousand grams of water. In the second column under $m^{\frac{1}{3}}$, for convenience in plotting curves, are tabulated the cube roots of the concentrations; the third column, R, shows the measured resistances of the solutions; next comes $k/m = \mu$, the equivalent conductivities; and finally, in the last column, are placed the ratios of μ to its value at infinite dilution, which was estimated from the former set of experiments. It was thought advisable, in view of the freezing point observations now being conducted in Dr. Griffiths' apparatus by Mr. T. G. Bedford, to include magnesium sulphate in the investigation. This substance was not examined in the platinum cell, so that it was necessary to extend the experiments to very dilute solutions. This was done in cell No. 1, which is made of Jena glass, and therefore is not likely to react appreciably with a solution of the nature of magnesium sulphate.

Potassium Chloride I. KCl = 74·59.

In Cell No. 2, the water used had a resistance of $8\cdot3 \times 10^6$ ohms at 0°.

| <i>m.</i> | <i>m</i> ^½ . | R. | <i>k/m</i> = <i>μ.</i> | <i>μ/μ_∞</i> . |
|-----------|-------------------------|-------|------------------------|--------------------------|
| 0·02393 | 0·288 | 7894 | 755 | 0·936 |
| 0·04261 | 0·349 | 4504 | 744 | 0·922 |
| 0·07924 | 0·430 | 2475 | 728 | 0·902 |
| 0·1459 | 0·526 | 1374 | 712 | 0·883 |
| 0·2441 | 0·625 | 835·4 | 701 | 0·868 |
| 0·4268 | 0·753 | 484·3 | 691 | 0·857 |
| 0·6379 | 0·861 | 325·5 | 688 | 0·853 |
| 0·8924 | 0·963 | 232·3 | 689 | 0·854 |
| 1·0759 | 1·025 | 191·9 | 692 | 0·857 |

Potassium Chloride II. KCl = 74·59.

| <i>m.</i> | <i>m</i> ^½ . | R. | <i>k/m</i> = <i>μ.</i> | <i>μ/μ_∞</i> . |
|-----------|-------------------------|-------|------------------------|--------------------------|
| 0·02394 | 0·288 | 7894 | 754 | 0·934 |
| 0·04275 | 0·350 | 4504 | 741 | 0·919 |
| 0·07971 | 0·430 | 2475 | 724 | 0·897 |
| 0·1475 | 0·528 | 1374 | 705 | 0·873 |
| 0·2486 | 0·629 | 835·4 | 688 | 0·852 |
| 0·4408 | 0·761 | 484·3 | 669 | 0·829 |
| 0·6697 | 0·875 | 325·5 | 655 | 0·812 |
| 0·9575 | 0·986 | 232·3 | 642 | 0·796 |
| 1·1697 | 1·054 | 191·9 | 636 | 0·789 |

Barium Chloride. $\frac{1}{2}\text{BaCl}_2$ = 104·1.

In Cell No. 2, the water used had a resistance of $8\cdot5 \times 10^6$ ohms.

| <i>m.</i> | <i>m</i> ^½ . | R. | <i>k/m</i> = <i>μ.</i> | <i>μ/μ_∞</i> . |
|-----------|-------------------------|-------|------------------------|--------------------------|
| 0·02040 | 0·273 | 10856 | 644 | 0·863 |
| 0·05112 | 0·371 | 4584 | 609 | 0·816 |
| 0·1137 | 0·485 | 2178 | 577 | 0·773 |
| 0·2377 | 0·619 | 1095 | 549 | 0·735 |
| 0·4705 | 0·778 | 580·4 | 523 | 0·700 |
| 0·8710 | 0·955 | 325·5 | 504 | 0·674 |
| 1·741 | 1·203 | 172·2 | 476 | 0·638 |

Copper Sulphate. $\frac{1}{2}\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ = 124·87.

Cell No. 2. The water had a resistance of $6\cdot6 \times 10^6$ ohms.

| <i>m.</i> | <i>m</i> ^½ . | R. | <i>k/m</i> = <i>μ.</i> | <i>μ/μ_∞</i> . |
|-----------|-------------------------|-------|------------------------|--------------------------|
| 0·02174 | 0·279 | 17173 | 382 | 0·548 |
| 0·07607 | 0·423 | 6397 | 293 | 0·421 |
| 0·2681 | 0·645 | 2359 | 226 | 0·324 |
| 0·5608 | 0·825 | 1313 | 193·9 | 0·279 |
| 0·8440 | 0·945 | 951·5 | 161·1 | 0·231 |
| 1·954 | 1·250 | 535·7 | 136·4 | 0·196 |

Potassium Bichromate. $\frac{1}{2}\text{K}_2\text{Cr}_2\text{O}_7 = 147 \cdot 3$.

In Cell No. 1, the water used had a resistance of $7 \cdot 26 \times 10^5$ ohms.

| <i>m.</i> | <i>m</i> ^½ . | R. | <i>k/m</i> = μ . | μ/μ_∞ . |
|-----------|-------------------------|--------|----------------------|--------------------|
| 0.002278 | 0.132 | 3004 | 710 | 0.865 |
| 0.006047 | 0.182 | 1138 | 706 | 0.860 |
| 0.01475 | 0.245 | 472.2 | 698 | 0.850 |
| 0.04019 | 0.343 | 5240* | 678 | 0.826 |
| 0.1010 | 0.466 | 2202* | 642 | 0.782 |
| 0.2577 | 0.636 | 917.1* | 604 | 0.736 |

Magnesium Sulphate. $\frac{1}{2}\text{MgSO}_4 \cdot 7\text{H}_2\text{O} = 123 \cdot 26$.

In Cell No. 1, the water used had a resistance of $9 \cdot 75 \times 10^5$ ohms.

| <i>m.</i> | <i>m</i> ^½ . | R. | <i>k/m</i> = μ . | μ/μ_∞ . |
|------------|-------------------------|--------|----------------------|--------------------|
| 0.00000644 | 0.0186 | 511000 | 702 | 0.987 |
| 0.00001398 | 0.0241 | 330000 | 697 | 0.980 |
| 0.00003218 | 0.0318 | 179200 | 687 | 0.965 |
| 0.00007707 | 0.0426 | 84710 | 680 | 0.955 |
| 0.0003438 | 0.0701 | 21230 | 652 | 0.916 |
| 0.001423 | 0.113 | 5554 | 598 | 0.840 |
| 0.005030 | 0.171 | 1881 | 513 | 0.721 |
| 0.02678 | 0.299 | 456.8 | 397 | 0.558 |

Magnesium Sulphate. $\frac{1}{2}\text{MgSO}_4 \cdot 7\text{H}_2\text{O} = 123 \cdot 26$.

In Cell No. 2, the water used had a resistance of $8 \cdot 7 \times 10^6$ ohms.

| <i>m.</i> | <i>m</i> . | R. | <i>k/m</i> = μ . | μ/μ_∞ . |
|-----------|------------|--------|----------------------|--------------------|
| 0.04995 | 0.368 | 8067 | 354 | 0.498 |
| 0.1158 | 0.487 | 4083 | 302 | 0.425 |
| 0.2136 | 0.598 | 2494 | 268 | 0.377 |
| 0.3574 | 0.710 | 1654 | 241.5 | 0.340 |
| 0.6413 | 0.862 | 1052.5 | 211.6 | 0.298 |
| 1.189 | 1.060 | 682.2 | 176.1 | 0.248 |
| 1.812 | 1.220 | 540.8 | 145.7 | 0.205 |
| 2.642 | 1.383 | 488.4 | 110.7 | 0.1556 |
| 3.463 | 1.513 | 524.1 | 78.6 | 0.1105 |

In order to obtain the most probable results for the ratio of the equivalent conductivities to their values at infinite dilution, curves were drawn on squared paper between *m*^½ and *k/m*, and the smoothed readings taken at the required places. It is usual to call this ratio the coefficient of ionization, but at the high concentrations here dealt

* In Cell No. 2.

with, we cannot assume that it really gives the fraction of the number of the molecules which are at any moment ionized; in the light of probable changes in the ionic fluidity of the liquids, and of the possible existence of complex ions, such an assumption is clearly unjustified. For the sake of convenience, the results previously obtained, as well as those of the experiments now described, are collected in the following table:—

Equivalent Conductivities at 0° referred to the Limiting Value
as Unity.

m = Number of Gram-equivalents of Solute per thousand grams of Solution.

| $m.$ | $m_{\frac{1}{2}}$. | KCl. | $\frac{1}{2}$ BaCl ₂ . | $\frac{1}{2}$ K ₂ Cr ₂ O ₇ . | $\frac{1}{2}$ CuSO ₄ . | $\frac{1}{2}$ MgSO ₄ . |
|---------|---------------------|-------|-----------------------------------|---|-----------------------------------|-----------------------------------|
| 0·00001 | 0·0215 | 1·000 | 1·000 | 0·991 | 0·998 | 0·983 |
| 0·00002 | 0·0272 | 1·000 | 1·000 | 0·980 | 0·993 | 0·976 |
| 0·00005 | 0·0368 | 1·000 | 0·998 | 0·952 | 0·981 | 0·963 |
| 0·0001 | 0·0464 | 0·999 | 0·995 | 0·929 | 0·967 | 0·950 |
| 0·0002 | 0·0585 | 0·998 | 0·990 | 0·902 | 0·947 | 0·932 |
| 0·0005 | 0·0794 | 0·996 | 0·980 | 0·880 | 0·908 | 0·899 |
| 0·001 | 0·100 | 0·992 | 0·969 | 0·870 | 0·863 | 0·864 |
| 0·002 | 0·126 | 0·987 | 0·953 | 0·864 | 0·807 | 0·814 |
| 0·005 | 0·171 | 0·976 | 0·925 | 0·863 | 0·717 | 0·720 |
| 0·01 | 0·215 | 0·962 | 0·896 | 0·858 | 0·638 | 0·659 |
| 0·02 | 0·271 | 0·944 | 0·864 | 0·847 | 0·557 | 0·587 |
| 0·03 | 0·311 | 0·932 | 0·843 | 0·834 | 0·512 | 0·545 |
| 0·05 | 0·368 | 0·917 | 0·813 | 0·815 | 0·468 | 0·497 |
| 0·10 | 0·464 | 0·896 | 0·778 | 0·783 | 0·405 | 0·435 |
| 0·20 | 0·585 | 0·874 | 0·742 | 0·749 | 0·348 | 0·380 |
| 0·40 | 0·737 | 0·858 | 0·710 | — | 0·294 | 0·322 |
| 0·50 | 0·794 | 0·855 | 0·699 | — | 0·275 | 0·313 |
| 1·0 | 1·000 | 0·856 | 0·665 | — | 2·230 | 0·264 |
| 1·2 | 1·063 | 0·860 | 0·657 | — | 0·218 | 0·248 |
| 1·5 | 1·145 | — | 0·645 | — | 0·208 | 0·227 |
| 2·0 | 1·260 | — | 0·632 | — | 0·194 | 0·192 |
| 3·0 | 1·442 | — | — | — | — | 0·133 |

In the earlier set of experiments, approximate values only were obtained for the absolute equivalent conductivities, changes in the adjustment of the platinum cell between the experiments on each salt causing a slight uncertainty in the cell constant. From the values of the constants of the glass cells now used, it is possible to calculate throughout the whole range of concentration of both sets of observations the exact equivalent conductivities of the salts investigated. The results are given below, and are expressed in Kohlrausch's units, in which the electrical conductivities, measured in reciprocal ohms, are divided by the concentrations of the solutions, measured in gram-equivalents per cubic centimetre.

Equivalent Conductivities at 0° in Absolute Units.

m = number of Gram-equivalents of Solute per thousand grams of Solution.

| <i>m.</i> | $m^{\frac{1}{2}}$. | KCl. | $\frac{1}{2}\text{BaCl}_2$. | $\frac{1}{2}\text{K}_2\text{Cr}_3\text{O}_7$. | $\frac{1}{2}\text{CuSO}_4$. | $\frac{1}{2}\text{MgSO}_4$. |
|-----------|---------------------|------|------------------------------|--|------------------------------|------------------------------|
| 0.00001 | 0.0215 | 807 | 746 | 813 | 696 | 699 |
| 0.00002 | 0.0272 | 807 | 746 | 804 | 692 | 694 |
| 0.00005 | 0.0368 | 807 | 745 | 781 | 684 | 685 |
| 0.0001 | 0.0464 | 806 | 742 | 763 | 674 | 676 |
| 0.0002 | 0.0585 | 806 | 739 | 740 | 660 | 663 |
| 0.0005 | 0.0794 | 803 | 731 | 722 | 633 | 639 |
| 0.001 | 0.100 | 800 | 723 | 714 | 602 | 614 |
| 0.002 | 0.126 | 796 | 711 | 709 | 563 | 579 |
| 0.005 | 0.171 | 787 | 690 | 708 | 500 | 512 |
| 0.01 | 0.215 | 776 | 669 | 704 | 445 | 468 |
| 0.02 | 0.271 | 761 | 645 | 695 | 388 | 417 |
| 0.03 | 0.311 | 752 | 629 | 685 | 357 | 387 |
| 0.05 | 0.368 | 740 | 607 | 669 | 326 | 353 |
| 0.10 | 0.464 | 723 | 581 | 643 | 282 | 309 |
| 0.20 | 0.585 | 705 | 554 | 615 | 243 | 270 |
| 0.40 | 0.737 | 692 | 530 | — | 205 | 229 |
| 0.50 | 0.794 | 690 | 522 | — | 192 | 222 |
| 1.0 | 1.000 | 690 | 496 | — | 160 | 188 |
| 1.2 | 1.063 | 694 | 490 | — | 152 | 176 |
| 1.5 | 1.145 | — | 481 | — | 145 | 161 |
| 2.0 | 1.260 | — | 472 | — | 135 | 136 |
| 3.0 | 1.442 | — | — | — | — | 94.5 |

"The Resistance of the Ions and the Mechanical Friction of the Solvent." By FRIEDR. KOHLRAUSCH, Foreign Member R.S.
Received February 17,—Read March 5, 1903.

(Translated into English for Dr. Kohlrausch by Dr. L. Austin.)

Messrs. Bousfield and Lowry in their interesting paper, "The Influence of Temperature on the Conductivity of Electrolytic Solutions,"* have discussed a hypothesis recently advanced by me. In this I stated the probability that the conductivities of all aqueous solutions approach, with decreasing temperature, a zero value at about the same temperature, and that the cause of this phenomenon is to be looked for in the disappearance of the fluidity of water. This hypothesis was very briefly mentioned, as it were, in parenthesis, in the midst of the discussion of the numerical data which formed the main portion of the paper.†

* Bousfield and Lowry, 'Roy. Soc. Proc.,' vol. 70, p. 42, 1902.

† Kohlrausch, "Über den Temperatureinfluss auf das elektr. Leitvermögen von Lösungen, insbesondere auf die Beweglichkeit der einzelnen Ionen im Wasser," 'Sitz. Ber. Berlin Akad.,' 1901, p. 1028.